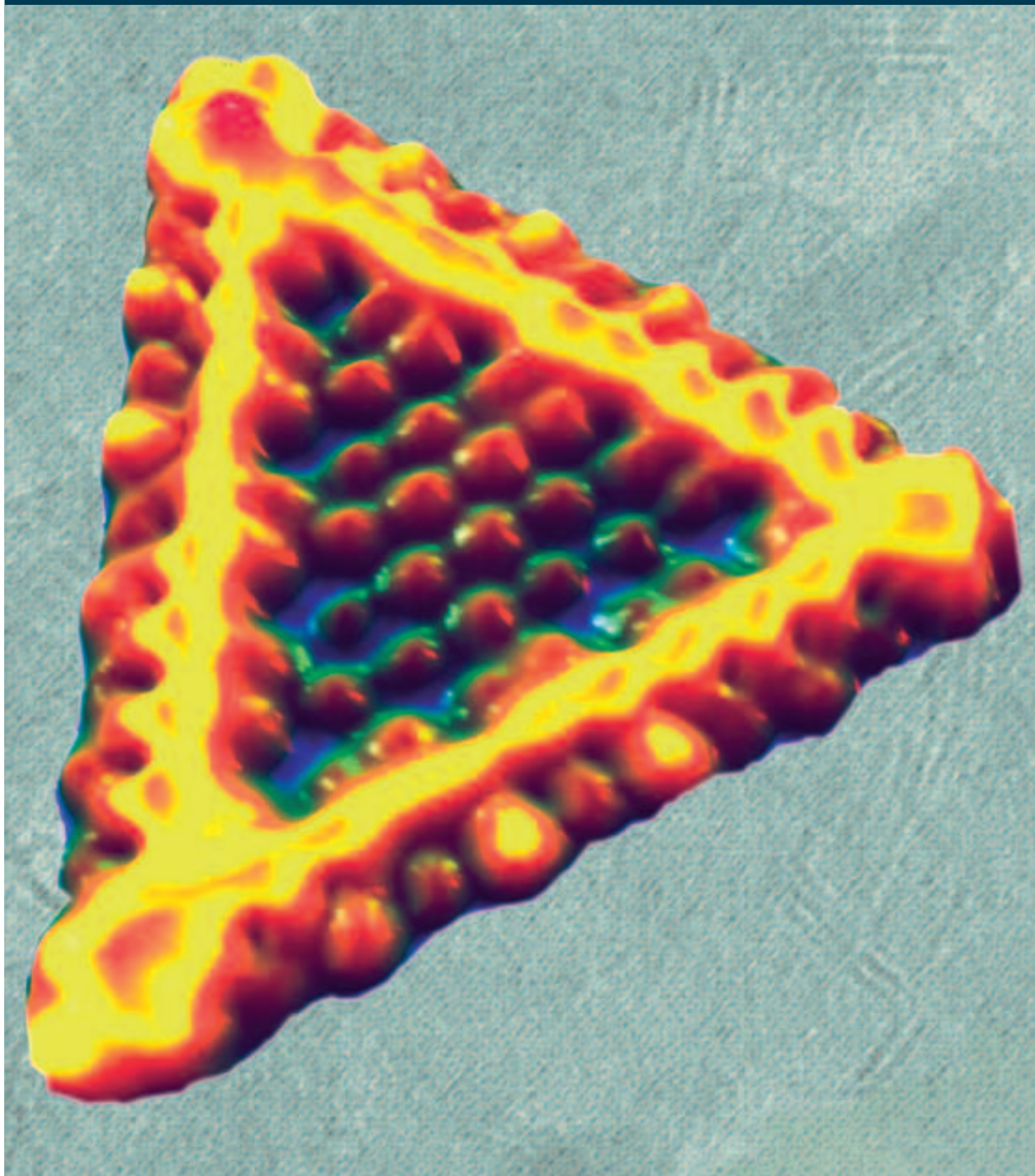


# FCC pretreatment catalysts

RESEARCH | TECHNOLOGY | CATALYSTS





# Improve your FCC pretreatment using BRIM™ technology

Topsøe has developed new FCC pretreatment catalysts using improved BRIM™ technology. The catalysts ensure outstanding performance as well as economic advantages.

## FCC pretreatment

FCC pretreatment technology effectively enhances the performance of the FCC unit and upgrades the properties of the FCC products.

Deep desulphurisation of FCC feed for the production of low sulphur gasoline is a very attractive alternative to the gasoline post-treatment technologies introduced in recent years.

FCC pretreatment with the latest generation of catalysts allows refiners to produce FCC feeds with 200 wt ppm sulphur, which will enable most refineries to produce 10 wt ppm sulphur gasoline.

With the current demands for diesel, an increasing number of pretreaters operate in high temperature mode in order to convert some of the VGO into diesel. Topsøe catalysts show high diesel selectivity in these types of applications and demonstrate excellent stability even at harsh conditions.

Topsøe's FCC pretreatment catalysts and processes have been designed to meet all the different requirements of the refiner. As such, they offer substantial economic advantages by improving FCC feed quality, resulting in an increased yield of the high value FCC unit products.

## Improved BRIM™ technology

In 2003 Topsøe introduced the first catalyst produced with the BRIM™ catalyst preparation technology. BRIM™ catalysts have been very well received by the industry, and now six years later the next generation of BRIM™ catalysts is ready, based on an improvement in the production technology.

Using the original BRIM™ technology, Topsøe found a way to both enhance the activity of the brim and Type II sites and to control the distribution between the two sites, as shown in figure 1.

The improved BRIM™ technology utilises an improvement in carrier technology to give lower density products with a better utilisation of the active metals, resulting in higher activities. The improved BRIM™ technology increases the dispersion of the active species on the carrier surface. By improving dispersion, the number of active sites for a given metal loading has been increased.

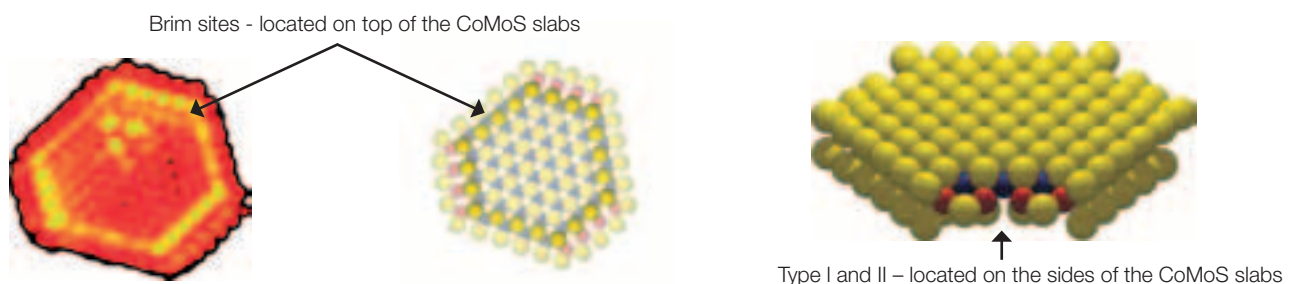


Figure 1: CoMos model. By use of Scanning Tunneling Microscopy (STM) it is possible – in atomic scale – to study the functionality of the active sites on a hydrotreating catalyst during the hydrotreating reactions. A new type of metallic brim sites close to the edges on the CoMoS slabs plays an important role in the hydrotreating reactions. The reaction sites for the direct desulphurisation are found on the sides of the CoMoS slabs.

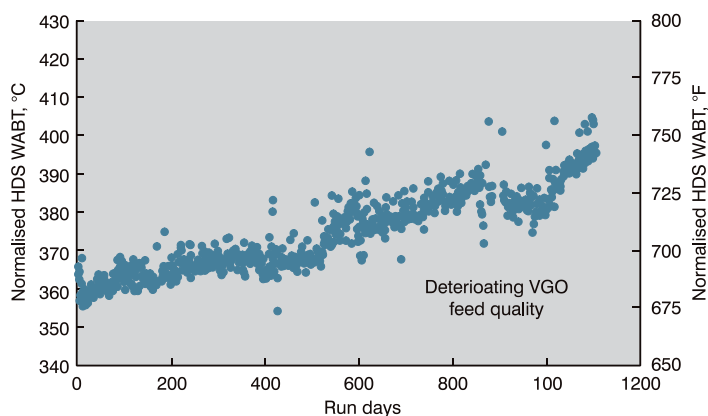


Figure 2: Normalised HDS reactor average temperature with TK-558 BRIM™ applied in low pressure FCC pretreater

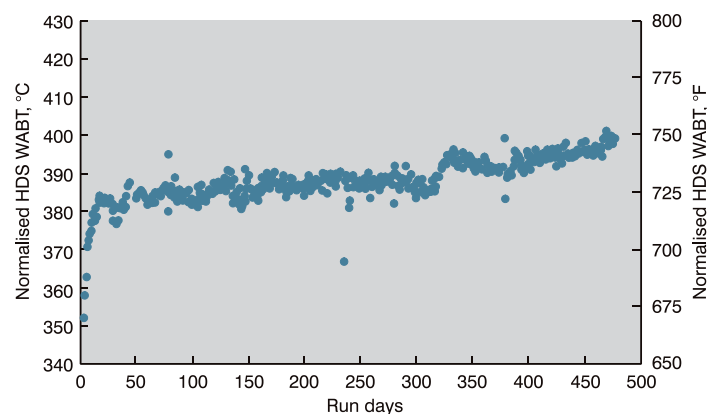


Figure 3: Normalised HDS reactor average temperature with TK-559 BRIM™ applied in high pressure FCC pretreater

## Topsøe FCC pretreatment catalysts

As the operation of each FCC pretreatment unit differs, the catalyst loading must be optimised to meet the refiner's objectives. In order to meet these needs Topsøe has developed a new generation of FCC pretreatment catalysts based on an improvement in our successful BRIM™ technology:

- TK-562 BRIM™
- TK-561 BRIM™
- TK-560 BRIM™

**TK-562 BRIM™** is our new high activity CoMo catalyst which demonstrates 10% higher catalyst activity than TK-558 BRIM™ whilst maintaining the same excellent stability. TK-562 BRIM™ is offered when ultra high HDS activity is required. A characteristic of the BRIM™ technology is that the activity for nitrogen removal is also very high for our CoMo catalysts.

**TK-561 BRIM™** is our new high activity NiMo catalyst with similar activity and stability to TK-559 BRIM™, but with lower filling density. TK-561 BRIM™ is an excellent catalyst for hydrodenitrogenation. The activity for nitrogen removal has been maximised whilst maintaining a high HDS activity.

**TK-560 BRIM™** is a high activity CoMo catalyst with an activity and stability equal to that of TK-558 BRIM™, but with a lower metal loading and filling density. TK-560 BRIM™ is the ideal choice, where fill cost is as important as performance.

## Catalyst stability

Catalysts prepared with the BRIM™ technology have demonstrated absolutely unmatched stability. Figure 2 illustrates the stability of a TK-558 BRIM™ catalyst operating at 38 bar hydrogen pressure in a 60,000 BPSD FCC pretreater. The TK-558 BRIM™ pretreater catalyst reduces sulphur content in the FCC feed by 96% to give a product with 700 wt ppm S and provides an HDN conversion much higher than obtained with conventional CoMo catalysts.

This charge of BRIM™ catalyst has been in operation for more than three consecutive years, which is a record for this unit. The stable operation of TK-558 BRIM™ at this low pressure is a true testament of the unmatched stability of BRIM™ catalysts.

Another charge of TK-559 BRIM™ catalyst has been in service in a mild hydrocracking unit operating at semi-high pressure of 90 bar, processing 28,000 barrels VGO per day. After 15 months of operation, the BRIM™ catalyst is performing excellently and produces low sulphur fuels for the diesel pool and feed for the FCC unit. The sulphur content in the diesel is in the 10-50 ppm range. The normalised HDS temperature in figure 3 shows extremely stable operation, which is remarkable when taking the severe conditions into consideration.

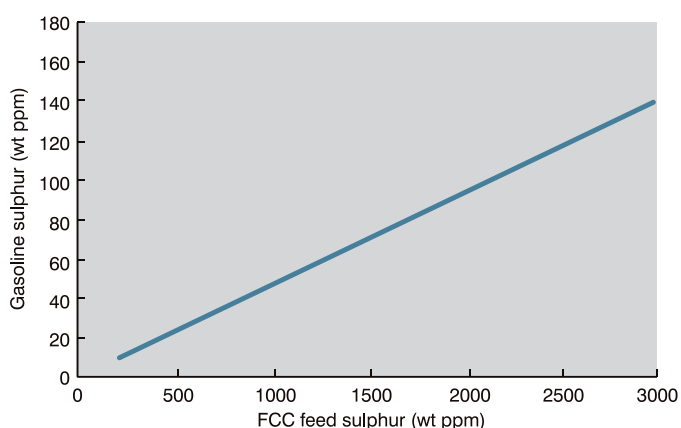


Figure 4: Lowering the sulphur content of the FCC feed is an effective way of producing low sulphur FCC gasoline

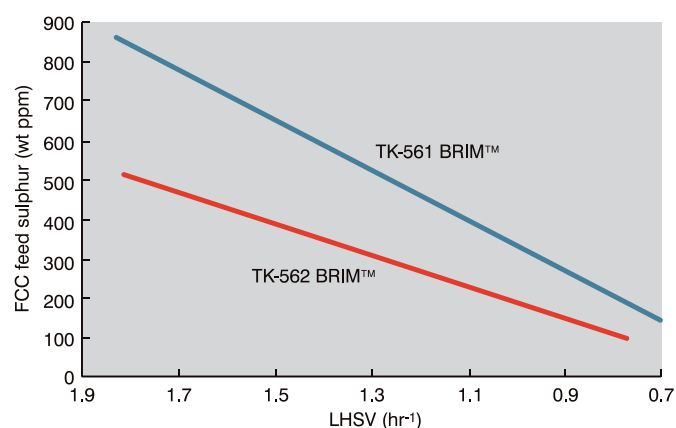


Figure 5: The high activity of TK-562 BRIM™ and TK-561 BRIM™ make it possible to reduce the sulphur content of the FCC feed to a very low level

## FCC pretreatment objectives

The main objectives of FCC pretreatment are typically sulphur removal (HDS) and nitrogen removal (HDN). However, apart from the considerations of HDS and HDN, it is also desirable to reduce the level of aromatic compounds, metals and Conradson Carbon.

There is a clear tendency in the market that more and more FCC pretreaters are running in a high-severity regime to meet clean fuels specifications, requiring more HDS while maintaining a high degree of HDN and reduction of polynuclear aromatics (PNA). Research at Topsøe's laboratories has consequently been directed towards development of new catalysts for FCC pretreatment with high denitrogenation and hydrogenation activities as well as increased desulphurisation activity.

### Sulphur removal

Hydrosulphurisation is important for two reasons: To lower the sulphur content of the FCC products and to limit emissions of SO<sub>x</sub> from the FCC regenerator.

FCC feed pretreatment is an excellent route to meet required sulphur levels in gasoline, e.g. by producing FCC feed with a sulphur content of 200-300 ppm S.

The gasoline sulphur specifications of 10 wt ppm in Europe and an average of 30 wt ppm in the US strongly affects the operating philosophy of the FCC and pretreating units. The FCC feedstock must then be hydrotreated to a sulphur level below 300-500 wt ppm (figure 4) to comply with the 10 wt ppm sulphur level and 700-900 wt ppm to comply with the 30 wt ppm sulphur level without investing in gasoline post-treatment technologies. Today, many refiners operate to such low product sulphur levels in order to produce ultra-low sulphur gasoline without post-treatment.

A higher operating temperature can be applied in the FCC pretreating unit to obtain improved sulphur removal. Existing units can be readily modified to meet future specifications by applying new catalysts with a higher activity and in some cases by adding reactor volume. Figure 5 shows that low VGO sulphur levels can be achieved by lowering LHSV. One of the major advantages of removing sulphur upstream the FCC unit is that there is no octane loss associated with the production of low sulphur FCC gasoline, as is the case with all post-treatment technologies.

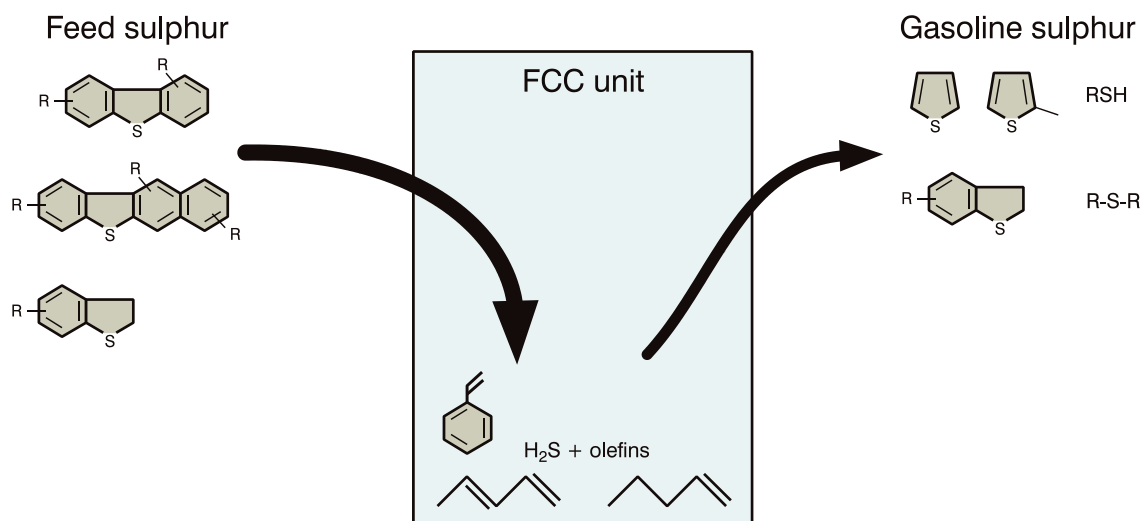


Figure 6: Reaction scheme for the transformation mechanism of organic sulphur compounds in the FCC unit

## Nitrogen removal

Nitrogen removal is an important aspect of FCC pretreatment. Nitrogen compounds in the FCC feed inhibit the FCC catalyst by neutralising the acid sites, thus reducing the activity of the FCC catalyst. This changes the selectivity of the FCC catalyst, resulting in a decreased yield of valuable gasoline product from the FCC unit. FCC pretreatment reduces the nitrogen content of the FCC feed and product. It is especially desirable to reduce the amount of basic nitrogen compounds, if light cycle oil is used for diesel production, since the presence of basic nitrogen compounds in light cycle oil strongly inhibits the HDS reaction in subsequent diesel desulphurisation.

## Reduction of aromatic compounds

A high degree of saturation of aromatic compounds in the FCC pretreatment step improves the yield and reduces the formation of coke in the FCC unit. This is because aromatic compounds are difficult to crack in the FCC unit, and the aromatic content is directly correlated to the amount of coke formed. If the aromatic compounds are instead converted into naphthenes in the pre-treatment step, they are easier to crack into valuable products in the FCC unit, and at the same time, less coke is produced.

## Metal removal and Conradson reduction

The removal of metals is especially important when relatively heavy feedstocks are treated, since the metal content of these feeds is typically higher. To further enhance metal removal in the FCC pretreater, a Topsøe grading consisting of hydrodemetallisation (HDM) catalysts will solve the above

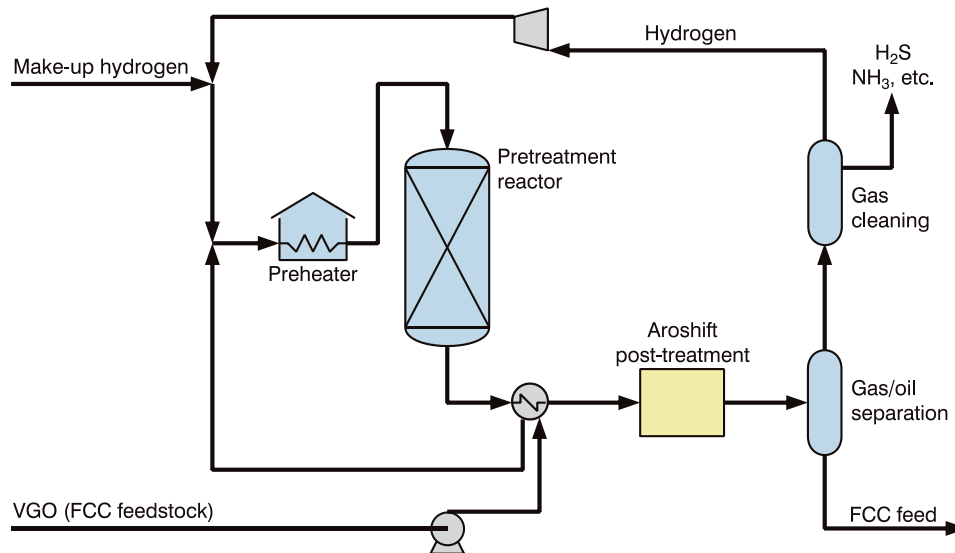
mentioned problems by providing a good HDM activity combined with a high metals capacity. The BRIM™ catalysts have demonstrated high tolerance for heavy metals, which is very unusual for this type of catalyst.

Reduction of Conradson Carbon in the FCC feed lowers the amount of coke formed, gives improved FCC catalyst selectivity and increases the crackability of the FCC feed. Both CoMo and NiMo catalysts can be applied, but normally a NiMo type like TK-561 BRIM™ would be the preferred choice due to the high hydrogenation activity.

## Arsenic removal

Catalyst poisoning by arsenic is a growing problem, as more of the crude, in particular Russian, Venezuelan and US West Coast crude, contains significant amounts of arsenic. Arsenic is known to be a very strong catalyst poison, and removal of the arsenic in the top of the pretreater is necessary in order to protect the main bed catalyst in the pretreater as well as any post-treatment catalyst.

To further enhance arsenic removal in the FCC pretreater, a Topsøe designed grading including an especially high capacity arsenic catalyst, TK-45 or TK-47, will solve this particular problem and protect the main bed catalysts from severe arsenic poisoning.



Topsøe Aroshift is a licensed technology that can be added as a low cost revamp to an existing FCC pretreater

## Improve the FCC pretreatment process with Topsøe Aroshift

To meet the latest, most stringent gasoline sulphur specifications (10 wt ppm in Europe and an average of 30 wt ppm in the US), the feed to the FCC units will have to be desulphurised to a degree that will make it necessary for existing FCC pretreaters to be operated at a very high severity (temperature). This will only be possible for some FCC pretreaters by increasing the catalyst (reactor) volume of the unit. High temperature operation of the FCC pretreater will significantly reduce the PNA saturation due to equilibrium, thus negatively impacting the profitability of the FCC unit.

Revamping existing FCC pretreaters using the Topsøe Aroshift Process will effectively reverse the negative effects of increased severity. Aroshift is a simple process comprising both technology and catalysts, which will lower the PNA content of the feed to the FCC unit. The Aroshift Process increases the FCC conversion, the yield of gasoline and of C3/C4 olefins, while reducing the amount of light and heavy cycle oil. Moreover, the quality of the FCC gasoline is improved. The benefits of applying the Topsøe Aroshift Process are even more pronounced for FCC pretreaters operating in mild hydrocracking mode since the reactor operating temperatures are much higher in mild hydrocracking service than in normal FCC pretreatment service.

## The Topsøe refining portfolio

In addition to our technology and catalysts for hydrocracking and hydrotreating, Topsøe has developed other related refinery technologies such as sulphur management, hydrogen production, NO<sub>x</sub> reduction (DeNO<sub>x</sub>), sulphur reduction (WSA) as well as combined reduction of NO<sub>x</sub> and SO<sub>x</sub> (SNOX™).

Topsøe integrates catalyst development and process technology development, which enable us to offer our clients a more complete package that is optimised from both a catalyst, technology and hardware standpoint.

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The information and recommendations have been prepared by Topsøe specialists having a thorough knowledge of the catalysts. However, any operation instructions should be considered to be of a general nature and we cannot assume any liability for upsets or damage of the customer's plants or personnel. Nothing herein is to be construed as recommending any practice or any product in violation of any patent, law or regulation.